Gulf Coast Research Center for Evacuation and Transportation Resiliency

LSU / UNO University Transportation Center

Improving the Self-Healing Properties of Concrete Materials by using Composite Actions with Fiber Reinforced Polymers

Final Report

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GULF COAST RESEARCH CENTER FOR EVACUATION AND TRANSPORTATION RESILIENCY

The Gulf Coast Research Center for Evacuation and Transportation Resiliency is a collaborative effort between the Louisiana State University Department of Civil and Environmental Engineering and the University of New Orleans' Department of Planning and Urban Studies. The theme of the LSU-UNO Center is focused on Evacuation and Transportation Resiliency in an effort to address the multitude of issues that impact transportation processes under emergency conditions such as evacuation and other types of major events. This area of research also addresses the need to develop and maintain the ability of transportation systems to economically, efficiently, and safely respond to the changing demands that may be placed upon them.

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The Center focuses on addressing the multitude of issues that impact transportation processes under emergency conditions such as evacuation and other types of major events as well as the need to develop and maintain the ability of transportation systems to economically, efficiently, and safely respond to the changing conditions and demands that may be placed upon them. Work in this area include the development of modeling and analysis techniques; innovative design and control strategies; and travel demand estimation and planning methods that can be used to predict and improve travel under periods of immediate and overwhelming demand. In addition to detailed analysis of emergency transportation processes, The Center provides support for the broader study of transportation resiliency. This includes work on the key components of redundant transportation systems, analysis of congestion in relation to resiliency, impact of climate change and peak oil, provision of transportation options, and transportation finance. The scope of the work stretches over several different modes including auto, transit, maritime, and non-motorized.

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Executive Summary

Background and Objectives

The aging civil infrastructure in the US represents a serious challenge for maintenance and repair using only limited available resources. For example, the average age of a bridge in the US is 43 years, with a design lifetime usually assumed equal to 50 years. The American Association of State Highway and Transportation Officials (AASHTO) estimated that the cost to repair every deficient bridge in the country would be approximately $140 billion. This repair cost does not include the cost associated with mandated annual bridge inspections, or the cost associated with traffic restrictions on structurally-deficient or functionally obsolete bridges. Immediate improvement of this situation is difficult due to the economic crisis that the US has suffered in recent years. It is envisioned that a long-term solution of this problem can only be achieved through new and creative transformative approaches that can significantly reduce the costs associated with inspection, maintenance, and repair of infrastructure elements. One solution for this problem involves the use of a new paradigm known as "self-healing concrete." Self-healing in concrete can be defined as the ability of concrete to autonomously heal cracks that may develop throughout its structure. By incorporating self-healing properties into concrete mixes, it is expected that concrete quality design and control methods will improve, with the goal of positively impacting concrete construction processes as a whole.

The specific objectives of this study were: (1) to evaluate the effects of preparation parameters (namely, temperature, agitation rate, and pH) on the shell thickness and size (diameter) of microcapsules of healing agents for use in self-healing concrete; (2) to evaluate the effects of microcapsules' shell thickness and size diameters on the concrete self-healing mechanism; and (3) to test the hypothesis that composite action due to FRP confinement of cylindrical concrete specimens can improve the self-repairing properties of self-healing concrete materials.

The goal of this research was to significantly advance the self-repairing capability of RC bridge components and systems. This capability is currently limited to the closure of small surface cracks produced in a controlled environment. This self-healing property mimics the self-healing of human skin after small cuts. The composite action due to confinement with fiber reinforced polymers (FRPs) can help close larger cracks in the concrete. In comparison with the human body, this self-healing capability is equivalent to the cicatrization of deep cuts and the healing of bone fractures. This research explored a completely innovative and untested idea, since it represents the first attempt of using composite action to enhance the performance of self-healing concrete materials.

Research Outcomes and Results

Three sets of experimental tests were developed and performed to achieve the objectives of this research. Two healing agents were evaluated for the first two objectives of this study, i.e., dicyclopentadiene (DCPD) and sodium silicate. The use of sodium silicate was considered for

the third objective of this study. Based on the results of the experimental program, the following conclusions were made: (1) as the pH was reduced, the shell thickness increased for DCPD microcapsules and decreased for sodium silicate microcapsules; (2) the more uniform and coherent microcapsules were produced at a temperature of 55°C for both DCPD and sodium silicate healing agents; (3) an increase in agitation rate resulted in a decrease in the average diameter of the microcapsules for DCPD, while it minimally affected the diameter of sodium silicate microcapsules; (4) sodium silicate microcapsules were effective in repairing the concrete after cracking for contents equal or higher than 1% of cement weight, with the best performance obtained for 5% sodium silicate content; (5) FRP-confinement generally improved the strength and stiffness of the specimens. Additional research is needed to investigate the effects of FRP-confinement on stiffness recovery.

Other Project Outcomes:

Students support:

A PhD and a Master student were supported on this project. The PhD student Yueqiang Sui works under the supervision of the PI, Dr. Michele Barbato, and his PhD research is in progress.

The Master student was Lt. Cmdr. James Gilford III and he worked under the supervision of the Co-PI, Dr. Hassan. He was a US Naval officer. Gilford's tuition was provided by the US Navy but support for Gilford included building an experimental setup and all the supplies he needed to conduct his research. He graduated with a MSc. in Engineering Science in summer 2012 with the following thesis:

Gilford III, J. (2012). "Microencapsulation of self-healing concrete properties." Master thesis, Department of Engineering Science, LSU, Baton Rouge, LA.

Publications:

This project resulted in one Transportation Research Board (TRB) paper presented at the 92nd Annual Meeting and one ASCE journal paper currently under review:

Gilford III, J., Hassan, M.M., Rupnow, T., and, Barbato, M. (2013). "Evaluation of Microencapsulation of Dicyclopentadiene (DCPD) and Sodium Silicate for Self-Healing Concrete." Paper #13-1172, 92nd Transportation Research Board Annual meeting, National Research Council, Washington, D.C.

Gilford III, J., Hassan, M.M., Rupnow, T., Barbato, M., Okeil, A., and, Asadi, S. (2013). "DCPD and Sodium Silicate Microencapsulation for Self-Healing of Concrete." ASCE Journal of Materials in Civil Engineering, under review.

It is expected that the results of this research will be used to prepare an additional journal publication.

Proposals submitted:

The project produced preliminary data that allowed the team to submit the following collaborative NSF proposal between LSU and Texas A&M Kingsville to the division of CMMI, SMM:

COLLABORATIVE RESEARCH: A NEW GENERATION OF INFRASTRUCTURE ELEMENTS MIMICKING SELF-HEALING MECHANISMS OF LIVING ORGANISMS. PI: Dr. Marwa Hassan, Co-PI's Dr. Michele Barbato, & Dr. Ayman Okeil. Requested funding: $266,543. Status: Declined.

The PI and Co-PI intend to re-submit a modified version of the previous proposal with stronger focus on the material characterization and the chemical/mechanical interaction between microcapsules of self-healing agents and concrete.

Abstract

This research study is motivated by the need to reduce the costs of maintenance and repair of the aging transportation infrastructure in the US. The proposed approach is to use self-healing concrete. The objectives of this study were: (1) to evaluate the effects of preparation parameters (namely, temperature, agitation rate, and pH) on the shell thickness and size (diameter) of healing agent microcapsules used in self-healing concrete; (2) to evaluate the effects of these microcapsules' shell thicknesses and size diameters on the concrete self-healing mechanism; and (3) to test the hypothesis that composite action due to FRP confinement of cylindrical concrete specimens can improve the self-repairing properties of self-healing concrete materials. Two healing agents were evaluated for the first two objectives of this study, i.e., dicyclopentadiene (DCPD) and sodium silicate. The use of sodium silicate was considered for the third objective of this study. Based on the results of the experimental program, the following conclusions were made: (1) as the pH was reduced, the shell thickness increased for DCPD microcapsules and decreased for sodium silicate microcapsules; (2) the more uniform and coherent microcapsules were produced at a temperature of 55°C for both DCPD and sodium silicate healing agents; (3) an increase in agitation rate resulted in a decrease in the average diameter of the microcapsules for DCPD, while it minimally affected the diameter of sodium silicate microcapsules; (4) sodium silicate microcapsules were effective in repairing the concrete after cracking for contents equal to or higher than 1% of cement weight, with the best performance obtained for 5% sodium silicate content; (5) FRP-confinement generally improved the strength and stiffness of the specimens. Additional research is needed to investigate the effects of FRP-confinement on stiffness recovery.

1 Introduction

The aging civil infrastructure in the US represents a serious challenge for maintenance and repair using only limited available resources. For example, the average age of a bridge in the US is 43 years, with a design lifetime usually assumed equal to 50 years. The American Association of State Highway and Transportation Officials (AASHTO) estimated that the cost to repair every deficient bridge in the country would be approximately $140 billion (AASHTO 2008). This repair cost does not include the cost associated with mandated annual bridge inspections, or the cost associated with traffic restrictions on structurally-deficient or functionally obsolete bridges. Immediate improvement of this situation is difficult due to the economic crisis that the US has suffered in recent years. It is envisioned that a long-term solution of this problem can only be achieved through new and creative transformative approaches that can significantly reduce the costs associated with inspection, maintenance, and repair of infrastructure elements. One solution for this problem involves the use of a new paradigm known as "self-healing concrete." Self-healing in concrete can be defined as the ability of concrete to autonomously heal cracks that may develop throughout its structure. By incorporating self-healing properties into concrete mixes, it is expected that concrete quality design and control methods will improve, with the goal of positively impacting concrete construction processes as a whole.

The main objective of this research project was to test the hypothesis that composite action in reinforced concrete (RC) structures can drastically improve the self-repairing properties of self-healing concrete materials. The goal of this research was to significantly advance the self-repairing capability of RC bridge components and systems. This capability is currently limited to the closure of small surface cracks produced in a controlled environment. This self-healing property mimics the self-healing of human skin after small cuts. The composite action due to confinement with fiber reinforced polymers (FRPs) can help close larger cracks in the concrete. In comparison with the human body, this self-healing capability is equivalent to the cicatrization of deep cuts and the healing of bone fractures. This research explored a completely innovative and untested idea, since it represents the first attempt of using composite action to enhance the performance of self-healing concrete materials.

2 Literature Review

Considerable interest has been given in recent years to the utilization of self-healing materials in concrete (Sharp and Clemena 2004). This has led to the introduction of a new class of smart materials that have the ability to heal after damage. Self-healing applications in concrete have led to the introduction of bacteria-based self-healing concrete and microcapsule-based self-healing concrete. Bacteria-based self-healing concrete uses mineral-producing bacteria, which were found able to seal surface cracks (Jonkers 2011). The concept of microcapsule healing is based on a healing agent being encapsulated and embedded in the concrete. When the crack propagates and reaches the microcapsule, the capsule breaks and the healing agent is released into the crack to repair it. Self-healing concrete provides a proactive approach rather than a reactive

countermeasure for cracks that develop within concrete structures. Self-healing concrete materials have been proven effective in terms of reduction of permeability (Reinhardt and Jooss 2003), as well as recovery of strength and stiffness under controlled cracking of the material in laboratory conditions (Li et al. 1998). However, the results in field applications have not yet been as satisfactory, since it is very difficult to limit the size of the cracks in the concrete to less than 150 μm (size beyond which the self-healing mechanism cannot be activated, see Yang et al. 2009). An emerging research direction focused on improving the performance of self-healing concrete is the development of engineered cementitious composites that can limit the average crack size due to the intrinsic material properties (Yang et al. 2009).

Since their introduction in the 1950s, microencapsulation has been evaluated in numerous construction materials including mortar, lime, cement, marble, sealant, and paints (Boh and Sumiga 2008). It has also been patented and tested in the food, chemical, textile, and pharmaceutical industries. The most common mechanism to trigger microcapsule-healing is through external pressure, which ruptures the microcapsule and releases the healing agent from the core. Therefore, the microcapsule must be sufficiently stiff to remain intact during processing, concrete mixing, pouring, and setting but it must break during damage of the concrete. In addition, the microcapsule shell provides a protective barrier between the catalyst and the healing agent to prevent polymerization during the preparation of the composite. There are three main methods for preparation of microcapsules (Boh and Sumiga 2008): (1) the mechanical method, which mechanically applies the microcapsule around the healing agent; (2) the coacervation method, in which the microcapsule wall solidifies around a core made of the healing agent; and (3) the polymerization method where the healing agent is applied as an emulsion, which then solidifies at the interface between water and healing agent to form the microcapsule wall.

FRP composites have found increasingly numerous applications in structural engineering due to their high strength-to-weight and stiffness-to-weight ratios, high corrosion resistance, and potentially high durability (Einde et al. 2003). One of these applications is the confinement of reinforced concrete (RC) columns with FRP to improve their structural performance in terms of ultimate load bearing capacity and ductility (Nanni and Bradford 1995, Seible et al. 1997). FRP confinement of RC columns presents numerous advantages compared to other strengthening techniques, e.g., strengthening using steel jackets. Some of these advantages include small increase in structural size and weight, easy transportation, and good resistance to corrosion and other degradation processes due to harsh environmental conditions (Bakis et al. 2002). This strengthening method has been widely used in retrofitting of bridges and buildings in the past few decades (Flaga 2000, Pantelides et al. 2000, Mertz et al. 2003, Monti 2003, Motavalli and Czaderski 2007).

The use of FRP confinement for RC cylindrical columns derives from the fact that, when concrete is subjected to an axial compression load, the concrete tends to expand laterally and to load the FRP confining jacket in axial tension along the radial direction. Thus, the concrete core of the column becomes subjected to a three-dimensional (3-D) compressive stress condition, which can significantly increase the compressive strength and the ductility of otherwise brittle concrete. Similar behavior has been observed also for RC columns with square or rectangular cross-section, for which a lower level of efficiency can be reached due to the fact that the stress

in the FRP is not uniform. When subjected to an axial compression load, FRP-confined RC columns behave differently than steel-confined RC columns. In fact, while steel jackets provide a constant confinement after the yielding point of the material is reached, FRP jackets provide a linearly increasing confinement force, which better contrasts the expansion of the concrete in the radial direction and significantly reduces the volumetric expansion of the concrete. This phenomenon produces a significantly more ductile behavior of the concrete, which is evidenced by the distinct bilinear shape of the monotonic stress-strain curve, with a smooth transition zone beginning at a stress level close to the strength of the unconfined concrete. It is noticed here that, while extensive research is available to document the positive effects on strength and ductility due to FRP confinement of RC columns subjected to axial and bending actions, no information is available in literature regarding the effects of FRP confinement on self-healing concrete.

3 Methodology

This research consisted of three main tasks: (1) evaluation of the effects of self-healing microcapsules' preparation parameters, namely, temperature, agitation rate, and pH on the shell thickness and size (diameter) of the microcapsules; (2) evaluation of the effects of microcapsules' shell thickness and size diameters on the concrete self-healing mechanism through mechanical experimental testing performed in laboratory; and (3) verification of the hypothesis that composite action due to FRP confinement of cylindrical concrete specimens can improve the self-repairing properties of self-healing concrete materials through mechanical experimental testing performed in laboratory.

3.1 Task 1: Evaluation of the effects of preparation parameters of self-healing microcapsules

There are three main methods for preparation of microcapsules (Boh and Sumiga 2008): (1) the mechanical method, which mechanically applies the microcapsule around the healing agent; (2) the coacervation method, in which the microcapsule wall solidifies around a core made of the healing agent; and (3) the polymerization method where the healing agent is applied as an emulsion, which then solidifies at the interface between water and healing agent to form the microcapsule wall. The polymerization method, which was used in this study, is categorized as either in-situ polymerization, in which the healing agent is added to the liquid phase of an emulsion, or as interfacial polymerization, in which the healing agent is dissolved into the liquid phase. In this study, in-situ polymerization was selected for preparation of the microcapsules.

As shown in Figure 1, the two main design parameters of interest during microcapsule preparation are shell thickness and microcapsule size (diameter). Microcapsule walls that are too thin would fail during the manufacturing process, concrete mixing, pouring, and setting (Tseng et al. 2005). In contrast, capsule shells that are too thick will not allow breaking or fracturing of the shell as the crack penetrates through the microcapsules plane. A well-developed process of microencapsulation using the urea-formaldehyde method was developed by Brown et al. (2003). The in-situ encapsulation method for water-immiscible liquids, by the reaction of urea with

formaldehyde at acid pH (Dietrich et al. 1989), is the foundation of the preparation method used in this study.

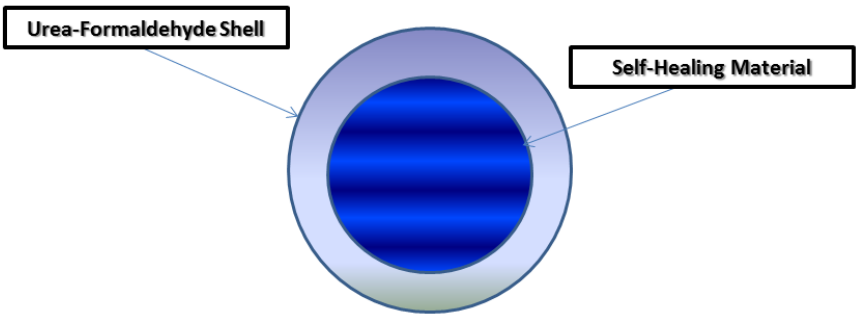


Figure 1: Schematic of the Components of a Microcapsule

Two healing agents were evaluated in this study, i.e., dicyclopentadiene (DCPD) and sodium silicate. DCPD ($C_{10}H_{12}$) is a white crystalline solid/clear liquid solution (depending on its potency) with an energy density of approximately 10,975 Wh/l. Its main use within industry and private practice is for resins/unsaturated polyester resins (Li et al. 2005). This chemical can be used as a monomer in polymerization reactions, such as ring-opening metathesis polymerization or olefin polymerization. Sodium silicate (Na_2O_3Si), which is also known as liquid glass, is a sodium metasilicate compound. This solid or aqueous solution is used in concrete applications to reduce its porosity. When added, a chemical reaction occurs with the excess of $CaOH_2$, which is already present in concrete (Greenwood et al. 1997). When sodium silicate reacts with $CaOH_2$, the concrete permanently binds with the silicates at the surface. This results in the product being a great sealer as well as a great water-repellent. Although theoretically possible, micro-encapsulation of sodium silicate using the urea-formaldehyde method has never been successfully accomplished before. White et al. (2001) were able to streamline the microencapsulation of DCPD by controlling its diameter as well as its morphology (Kessler et al. 2003).

The microcapsule self-healing method has the ability to independently resolve issues such as internal cracking and micro-cracking. When a crack occurs, a path towards rapid deterioration that could lead to structural failure is possibly initiated. By filling these voids and cracks with self-healing materials, concrete structures can achieve a longer life cycle along with a reduced likelihood of damage from unwanted moisture and corrosion (Brown et al. 2003). Although DCPD is an exceptional healing agent alone, in order for the agent to achieve maximum effectiveness, an appropriate interaction is required to polymerize the healing agent within the damaged area. A process called Ring Opening Metathesis Polymerization (ROMP) is used to polymerize the healing agent. This process provides the following advantages for self-healing microcapsules (White et al. 2001): more durable shell life, low monomer viscosity and volatility, rapid polymerization during ambient conditions, and low shrinkage rate during polymerization.

ROMP utilizes a Grubbs catalyst (transition metal catalyst), which incorporates a high metathesis method. The use of this catalyst allows multiple chemical groups to be utilized within the chemical process (such as oxygen and water). When DCPD encounters the Grubbs catalyst, polymerization occurs (Brown et al. 2005). Sodium silicate, however, does not require a matrix and can be used as an individual healing component. The first reaction consists of sodium silicate reacting with calcium hydroxide, which is a product of cement hydration (Nonat 2004). The second reaction occurs between sodium hydroxide and silica. In both processes, the mending agent that resides in an aqueous environment within the microcapsule itself is essential (Nonat 2004). Water enables the hydration of the damaged cement paste and allows further bonding of the mending agent. The products of both reactions fill the crack and subsequently permit recovery of strength. Both processes support the presence of the aqueous mending agent, which also provides further integrity of the concrete by creating a bond and healing the crack (Brown et al. 2005).

3.1.1 Test materials

The chemicals utilized in the preparation of the microcapsules based on the in-situ polymerization method are presented in Table 1. The two microencapsulation laboratory procedures that were utilized in this study for preparation of DCPD and sodium silicate microcapsules are presented in Appendices A and B, respectively.

Table 1: Required chemicals for interfacial polymerization synthesis

Chemical	Function	Manufacturer
Urea	Creates endothermic reaction in water	The Science Company
Ammonium Chloride	Assists with curing Process	The Science Company
Resorcinol (Technical Grade Flake)	Reacts with formaldehyde and is a chemical intermediate for the synthesis process	NDSPEC Chemical Corporation
ZeMac E60 Copolymer	Improves mechanical properties	Vertellus Specialties, Inc.
ZeMac E400 Copolymer	Improves mechanical properties	Vertellus Specialties, Inc.
Octanol	Prevents surface bubbles	Oltchim
Hydrochloric Acid	Lowers pH	The Science Company
Sodium Silicate	Reacts with $Ca(OH)_2$	The Science Company
Sodium Hydroxide	Increases pH	The Science Company
Formaldehyde	Reacts with urea during synthesis process	The Science Company
Grubbs Catalyst	Reacts with DCPD and polymerizes	Materia, Inc.
DETA (diethylenetriamine) Mix with EPON 828	Used in synthesis of catalysts, epoxy curing agent, and corrosion inhibitors	Huntsmann
DCPD	Selected Resin to Heal Concrete Crack	Texmark- 87% & 89% Purity Cymetech- 99% Purity

3.1.2 Test methods

An experimental program was developed to evaluate the effects of preparation parameters (namely temperature, agitation rate, and pH) on the shell thickness and size of the microcapsules using Scanning Electron Microscopy (SEM). Microscopic analysis was conducted using a FEI Quanta 3D SEG Dual Beam SEM with focused ION beam at an acceleration voltage of 15kV

and in the Backscattered Electron Imaging Mode. The images were stored as 1,290×968 TIFF files. Using image analysis software (Image J), the average particle diameter and shell thickness was measured and calculated. Measured microcapsules were selected by random sampling from each developed batch. The samples were coated with a thin layer of platinum conducting film by sputtering. Each sample was sputtered for 4 minutes to ensure an even distribution of the coating around each shell.

Table 2 presents the experimental matrix followed in this task. Two healing agents were evaluated, i.e., DCPD and sodium silicate. During synthesis, the agitation rate, temperature, and pH were varied one at a time. The agitation rate was varied at six levels for the DCPD synthesis and at four levels for the sodium silicate synthesis, while the temperature and pH were kept constant. Similarly, to evaluate the effect of temperature, three levels were used for both DCPD and sodium silicate, while the pH and agitation rate were kept constant. Three pH levels were considered for both DCPD and sodium silicate, while the temperature and agitation rate were kept constant. The constant reference levels of temperature, pH, and agitation rate were: 55°C, 3.7, and 550 rpm, respectively, for the DCPD; and 55°C, 3.0, and 550 rpm, respectively, for the sodium silicate. This experimental matrix resulted in a total of 10 synthesis methods tested using DCPD and 8 synthesis methods tested using sodium silicate.

Table 2: Experimental test matrix for Task 1

Parameters	DCPD	Sodium silicate
Agitation rate	250, 350, 450, 550, 800, and 1000	250, 350, 450, and 550
Temperature	49, 52, and 55	51, 53, and 55
pH value	3.1, 3.4, and 3.7	3, 3.1, and 3.2

3.2 Task 2: Evaluation of the effects of microcapsules' properties on concrete self-healing mechanism

The incorporation of the prepared microcapsules in concrete's response to loading was evaluated in the laboratory. Concrete cylinder specimens with height equal to 8 in (20.32 cm) and diameter equal to 4 in (10.16 cm) were prepared using a standard ready-mix concrete with a water/cement ratio of 0.5 and a nominal compressive strength of 4,000 psi (28 MPa). Sodium silicate microcapsules, prepared at a pH value of 3.1, were added to the mixing water at a content of 0.5, 1.0, 2.5, and 5.0% by weight of cement. Sodium silicate microcapsules were also prepared at three pH values (3.0, 3.1, and 3.2) in order to vary the shell thickness and were added to the mixing water at a content of 5.0% by weight of cement. DCPD was used at a content of 0.25% by weight of cement for microcapsules prepared at a pH of 3.1, 3.4, and 3.7 to vary the shell thickness. The cylinders were steam-cured in a temperature and humidity-controlled chamber. The heat and moisture penetrated the specimens quickly, fully hydrated the concrete material, and strengthened the concrete cylinders so that they could be used directly after accelerated curing. Cylindrical concrete specimens were de-molded after 24 hours and were cured by applying steam curing at 20 to 25°C for six days.

Specimens were tested based on a modified version of ASTM C 469, Standard Test Method for Static Modulus of Elasticity and Poisson's Ratio of Concrete in Compression, by applying 70% of the peak concrete strength. The maximum load was increased to 70% of the peak strength instead of 40% as required in ASTM C 469 to induce damage in the concrete specimens and to observe the effect of the microcapsules on the healing process. Specimens were loaded and unloaded for three cycles and were then left in the curing room for 48 hours to heal. After the healing period, specimens were then retested using the same test protocol. The initial tangent modulus, which is defined as the slope of the tangent to the stress-strain curve at the origin, was calculated before and after healing. Three replicates were prepared for each testing condition with an average coefficient of variation of 10% in the modulus of elasticity.

3.3 Task 3: Evaluation of FRP-confinement effects on self-healing concrete

Based on the results obtained from Tasks 1 and 2, sodium silicate was investigated as the healing agent in Task 3. Optimum microcapsule preparation parameters (namely temperature, agitation rate, and pH) to control the shell thickness and size of the microcapsules were also chosen based on the results from Tasks 1 and 2 as: temperature = 55°C; agitation = 350 rpm; and pH = 3.1.

3.3.1 Test materials

The chemicals utilized in the preparation of the microcapsules using the in-situ polymerization method are listed in Table 1. The micro-encapsulation laboratory procedures that were utilized in this study for preparation of sodium silicate microcapsules are presented in Appendices A. The concrete utilized in this research was QUIKRETE Pro Finish high strength concrete mix, with a nominal compressive strength of 5,000 psi. The FRP sheet used was SikaWrap Hex-100G uniaxial E-glass fiber fabric designed specifically for structural strengthening. The properties of the fiber are listed in Table 2. SikaDur 300 impregnating resin was used as adhesive with a volume mixing ratio of A:B 2.82:1.

Table 3: Mechanical properties of the glass fiber reinforced polymer (SikaWrap Hex-100G)

Tensile Strength Ksi	Tensile Modulus Ksi	Elongation %	Density lbs./in.^{3}	Nominal Thickness in.
330	10,500	4	0.092	0.014

3.3.2 Experimental matrix

A total of 12 plain concrete and 18 self-healing concrete cylinders of 4-in (10.16 cm) diameter and 8-in (20.32 cm) height were prepared for uniaxial compression tests. For the plain concrete specimens, six specimens were left unconfined and six specimens were wrapped with one layer of FRP. For the self-healing concrete specimens, the content of sodium silicate microcapsules was varied as 1%, 2.5% and 5% of cement weight. Three unconfined specimens and three FRP-confined specimens were prepared for each level of sodium silicate content.

The concrete cylindrical specimens were prepared using the QUIKRETE Pro Finish concrete mix with a water/cement ratio of 0.5. Sodium silicate microcapsules were added to the mixing

water at a carefully measured content of 1.0, 2.5, and 5.0% by weight of cement. The cylinders were de-molded after 24 hours and submerged into water at a temperature between 20-25°C for 28 days to be fully cured. For the confined specimens, the concrete surface was carefully cleaned before being impregnated with the resin. One layer of glass fiber was fully impregnated with resin and then wrapped around the concrete cylinders with the glass fiber aligned along the hoop direction. To avoid anchorage rupture, an overlap length of a quarter of the circumference was adopted along the fiber direction, as recommended by the FRP producer.

Table 4 presents the test matrix followed in Task 3 of this research. The specimens are identified using acronyms composed by three parts. The first part of the acronym is composed by two characters that indicate the type of test, i.e., ST = strength test (each specimen was monotonically loaded until the peak strength was reached and the specimens failed) and SH = self-healing test (the undisturbed specimens were subjected to cyclic loading, then left to heal for one week, and then subjected to a second set of cycling loading). The second part of the acronym consists of two digits that indicate the sodium silicate content, i.e., 00 = 0.0% (ordinary concrete), 10 = 1.0% (self-healing concrete with sodium silicate content equal to 1% of cement weight), 25 = 2.5% (self-healing concrete with sodium silicate content equal to 2.5% of cement weight), 50 = 5.0% (self-healing concrete with sodium silicate content equal to 5% of cement weight). The third part of the acronym is composed by two or three characters that indicate the confinement type, i.e., PL = plain (unconfined) concrete and FRP = FRP-confined concrete.

Table 4: Experimental test matrix for Task 3

Test type	Specimen ID	SS content	Confinement type	Number of specimens
Strength test	ST00PL	0.0%	Plain	3
	ST00FRP		FRP	3
Self-healing test	SH00PL	0.0%	Plain	3
	SH00FRP		FRP	3
Self-healing test	SH10PL	1.0%	Plain	3
	SH10FRP		FRP	3
Self-healing test	SH25PL	2.5%	Plain	3
	SH25FRP		FRP	3
Self-healing test	SH50PL	5.0%	Plain	3
	SH50FRP		FRP	3

3.3.3 Loading test protocol

The strength test was conducted using an ELE ACCU-TEK TM 350 compression machine following the ASTM C39 standard (Standard Test Method for Compression Strength of Cylindrical Concrete Specimens). The self-healing test was performed in three phases: a first set of cyclic loading, a one-week period of self-healing during which the specimens were maintained in water between a temperature of 20°C to 25°C, and a second set of cyclic loading. The cyclic loading was performed using an MTS machine following a modified version of ASTM C469 (Standard Test Method for Static Modulus of Elasticity and Poisson's Ratio of Concrete in

Compression). The specimens were loaded and unloaded for one cycle up to 20% of their compressive strength (estimated from the results of the previously performed strength tests), one cycle up to 40% of their compressive strength, and then three cycles up to 75% of their compressive strength. The stress time history was recorded from a loading cell and the strain time history was calculated using an LVDT attached to the specimens through a compressometer. The tangent stiffness modulus (computed as the slope of the stress-strain curve between 2% and 10% of the estimated peak strength of the specimens) and the residual strain at end of each loading cycle (computed as the strain reached during unloading at 2% of the estimated peak strength of the specimens) were calculated before and after healing.

4 Results

4.1 Evaluation of the effects of preparation parameters of self-healing microcapsules

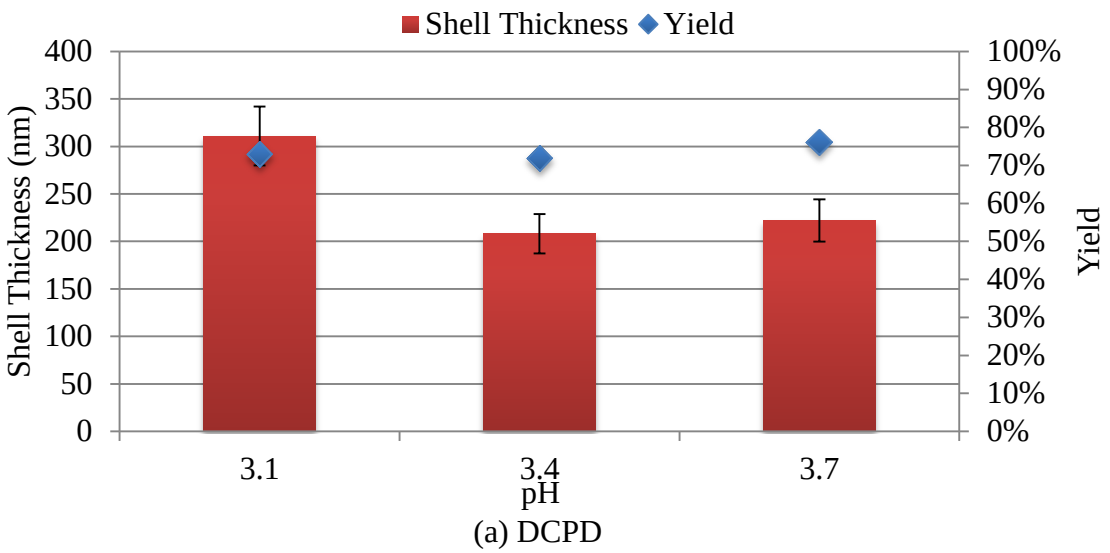
Numerous factors can affect the morphology, diameter, and shell thickness of the prepared microcapsules. Morphology, diameter, and shell thickness calculations were conducted based on image analysis of SEM images. Yield was calculated according to the following equation:

$$\%\text{Yield} = \frac{\text{Weight of microcapsules}}{\text{theoretical weight of ingredients}} \text{x}100 \quad (1)$$

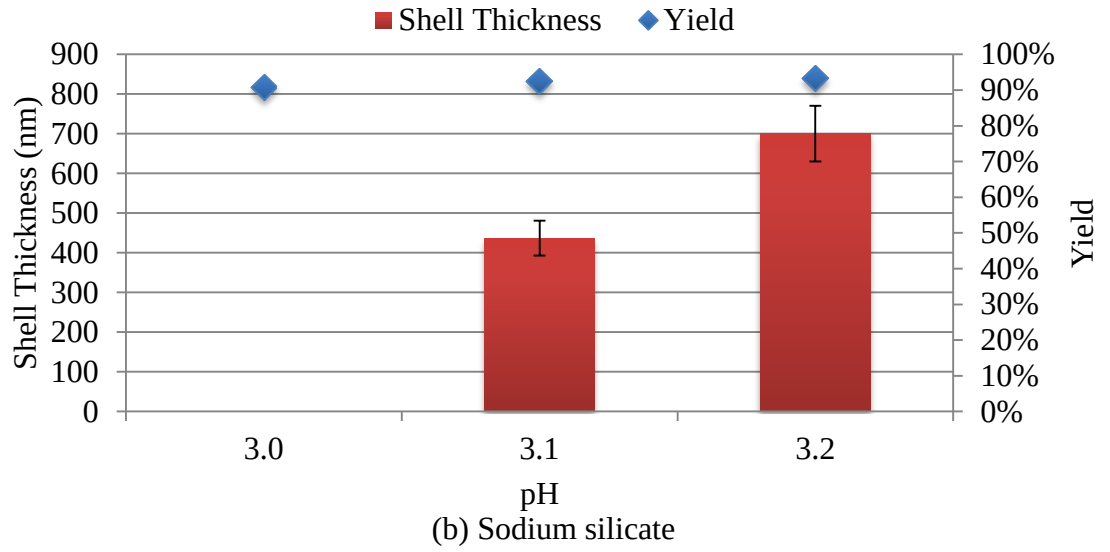
The highest yield for DCPD was 79.0% at an agitation rate of 350 rpm, temperature of 55°C, and a pH of 3.7. The highest yield for sodium silicate was 94.9% at an agitation rate of 350 rpm, a temperature of 55°C, and a pH of 3.2. The following Figures 2, 4, and 6 show the percent yield for DCPD and sodium silicate microcapsules as a function of pH, temperature, and agitation rate, respectively.

4.1.1 Effects of pH on morphology and shell thickness

Figure 2 presents the effects of pH on the shell thickness for DCPD (Figure 2(a)) and sodium silicate microcapsules (Figure 2(b)), respectively, in terms of mean (represented by the filled bar) and standard deviation (represented by the line bar as a ± one standard deviation) of the measured shell thicknesses.

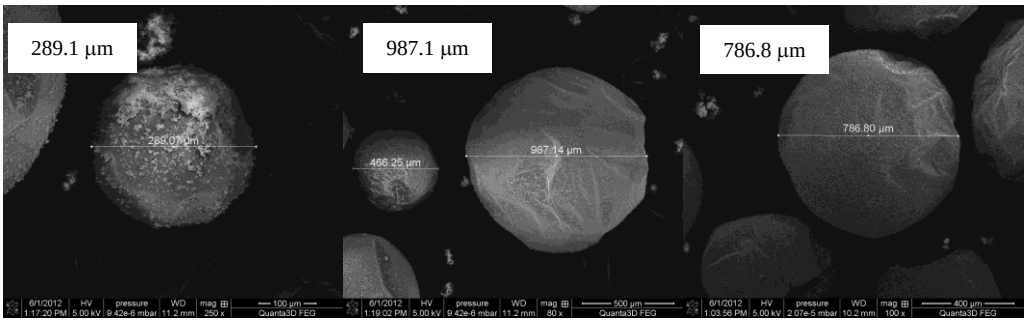


(a) DCPD

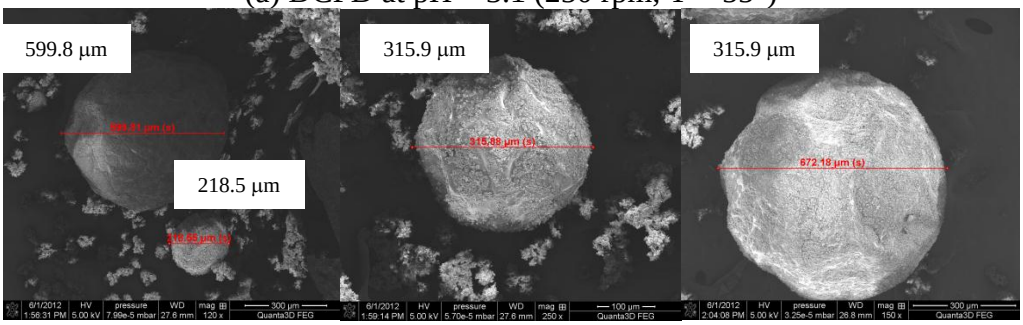


(b) Sodium silicate

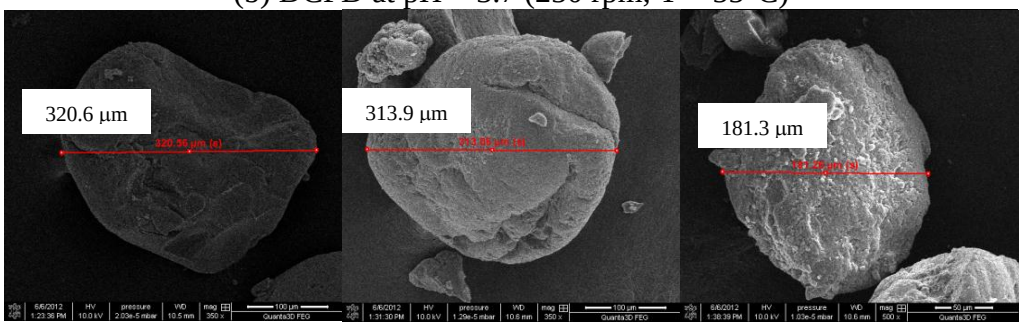
Figure 2: Effect of pH Values on the Shell Thickness for: (a) DCPD Microcapsules, and (b) Sodium Silicate Microcapsules



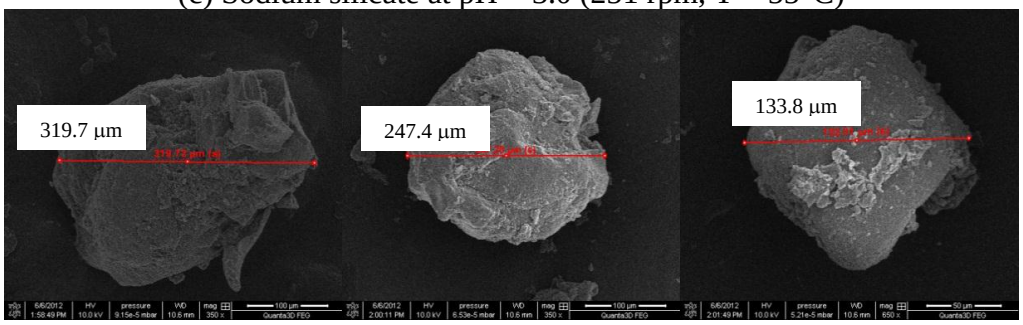
(a) DCPD at pH = 3.1 (250 rpm, T = 55°)



(b) DCPD at pH = 3.7 (250 rpm, T = 55°C)



(c) Sodium silicate at pH = 3.0 (251 rpm, T = 55°C)



(d) Sodium silicate at pH = 3.2 (255 rpm, T = 55°C)

Figure 3: Effect of pH Values on the Morphology of Microcapsules for: (a) DCPD at pH = 3.1, (b) DCPD at pH = 3.7, (c) Sodium Silicate at pH = 3.0, and (d) Sodium Silicate at pH = 3.2

Results shown in Figure 2(a) indicate that the increase in pH values resulted in an overall decrease in the shell thickness for DCPD, with a minimum mean shell thickness at a pH value of 3.4. As shown in Figure 2(b), the increase in pH values resulted in an increase in the shell thickness for sodium silicate. At a pH value of 3.0, the shell wall of the sodium silicate microcapsules became extremely thin and the microcapsules tended to collapse during the

measurements of their shell thickness. As a consequence, the measurement of the microcapsules' shell thickness was not possible. The maximum shell thickness of sodium silicate microcapsules was almost twice the maximum shell thickness of DCPD microcapsules. This phenomenon was due to sodium silicate being transformed into a gel like solution prior to microencapsulation. This gel solution made the compound much easier to encapsulate and produced a much stronger shell wall.

Figure 3 presents SEM images of the microcapsules prepared with DCPD and sodium silicate at different pH values. It is observed that the microcapsules prepared with DCPD were closer to a spherical shape and more uniform than the microcapsules prepared with sodium silicate. In addition, the size of the microcapsules was reduced as the pH value was increased. The outer surface of the microcapsules had a rough permeable layer, whereas the inside was smooth and free of cavities.

4.1.2 Effects of temperature

Figure 4 presents the effects of temperature on the shell thickness for DCPD (Figure 4(a)) and sodium silicate microcapsules (Figure 4(b)), respectively, in terms of mean (represented by the filled bar) and standard deviation (represented by the line bar as a ± one standard deviation) of the measured shell thicknesses. For the DCPD microcapsules at 49°C, the solution remained an emulsion and no encapsulation took place. For sodium silicate, there were no microcapsules formed at 53°C. Figure 5 presents SEM images of the microcapsules for DCPD (Figure 5(a) and (b)) and sodium silicate (Figure 5(c) and (d)) prepared at different temperatures. Also in this case, the microcapsules prepared with DCPD were with a shape closer to spherical and more uniform than the microcapsules prepared with sodium silicate. In addition, the size of the microcapsules was reduced as the temperature was increased.

4.1.3 Effects of agitation rate

Figure 6 shows the effect of agitation rate on the diameter of the microcapsules for DCPD (Figure 6(a)) and sodium silicate microcapsules (Figure 6(b)), respectively, in terms of mean (represented by the filled bar) and standard deviation (represented by the line bar as a ± one standard deviation) of the measured microcapsules' diameter. The increase in agitation rate resulted in a decrease of the average diameter of the microcapsules for DCPD. This is due to the large microcapsules being broken up into smaller ones when high shear (due to the centrifugal forces) is applied. The optimum size of the microcapsules is dependent on the crack size that is expected to be filled during the healing mechanism. On the other hand, the diameter of the microcapsules remained constant for sodium silicate microencapsulation as the agitation rate increased, as shown in Figure 6(b). This phenomenon may be attributed to the attempt to stabilize the alkalinity of the sodium silicate solution for the microencapsulation procedure using urea-formaldehyde. The SEM images presented in Figure 7 also show a reduction in diameter with the increase in agitation rate for DCPD. The same trend is observed in Figure 8, which provides SEM pictures of DCPD microcapsules produced at different agitation rates with a lower magnification rate compared with Figure 7, in order to show several DCPD microcapsules in a single picture and to provide a better idea of the size distribution observed for DCPD microcapsules.

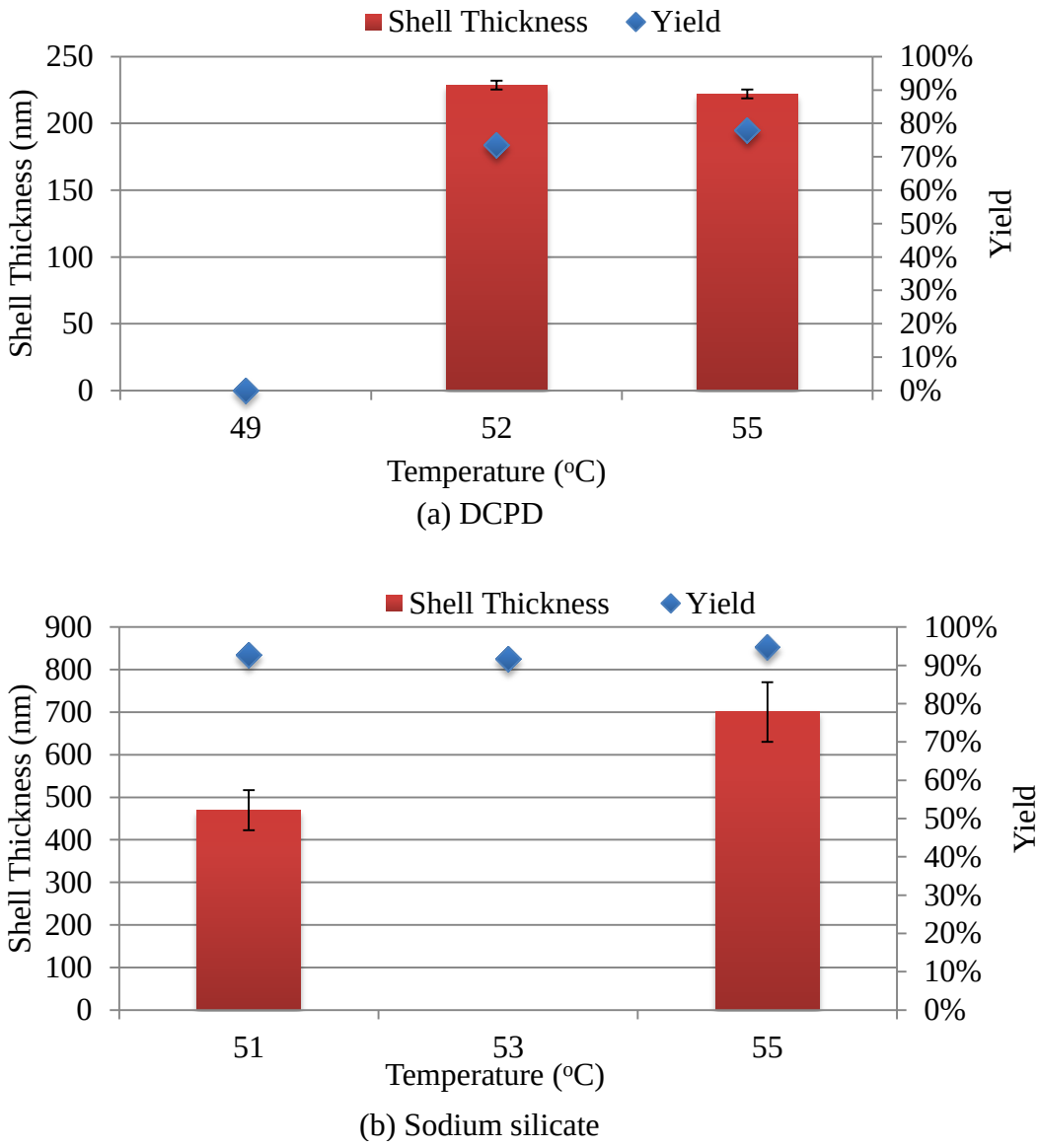
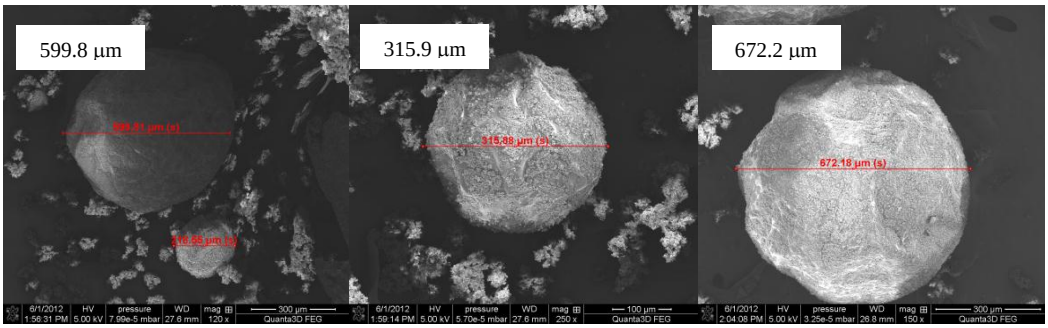
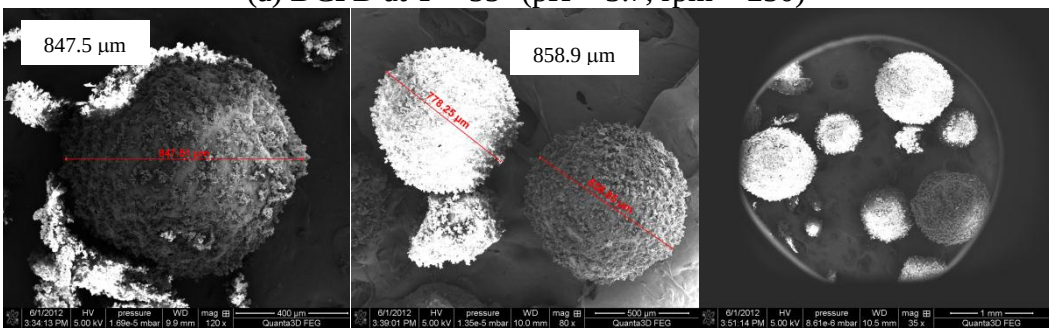


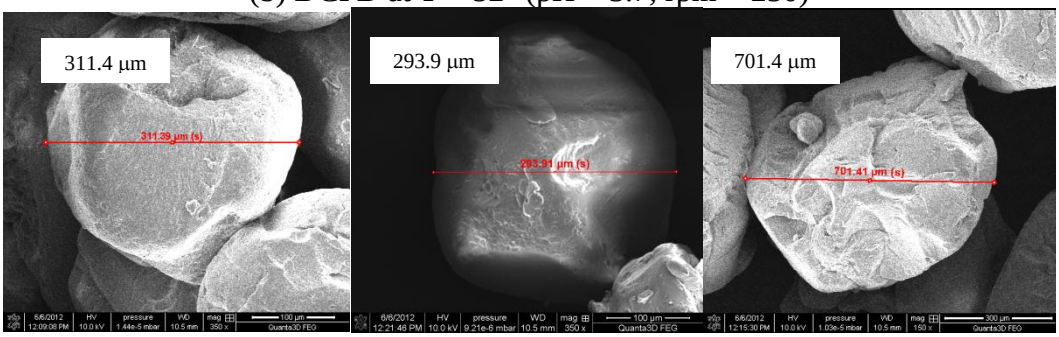
Figure 4: Effect of Temperature on the Shell Thickness for: (a) DCPD Microcapsules, and (b) Sodium Silicate Microcapsules



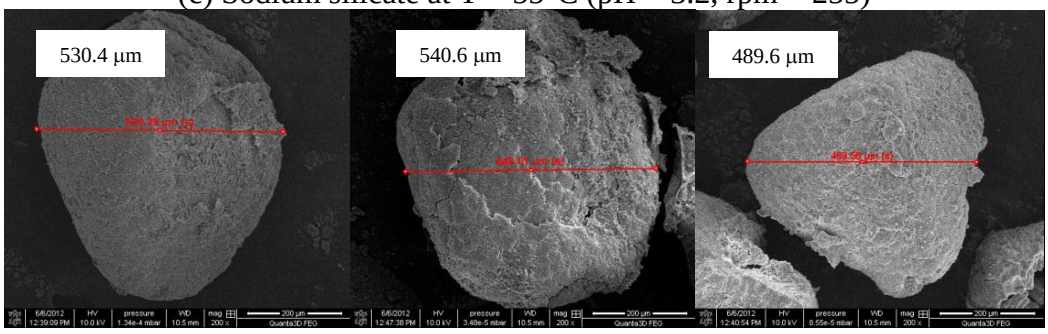
(a) DCPD at T = 55° (pH = 3.7, rpm = 250)



(b) DCPD at T = 52° (pH = 3.7, rpm = 250)



(c) Sodium silicate at T = 55°C (pH = 3.2, rpm = 255)



(d) Sodium silicate at T = 51°C (pH = 3.2, rpm = 255)

Figure 5: Effects of Temperature on the Morphology of Microcapsules for: (a) DCPD at T = 55°C, (b) DCPD at T = 52°C, (c) Sodium Silicate at T = 55°C, and (d) Sodium Silicate at T = 51°C

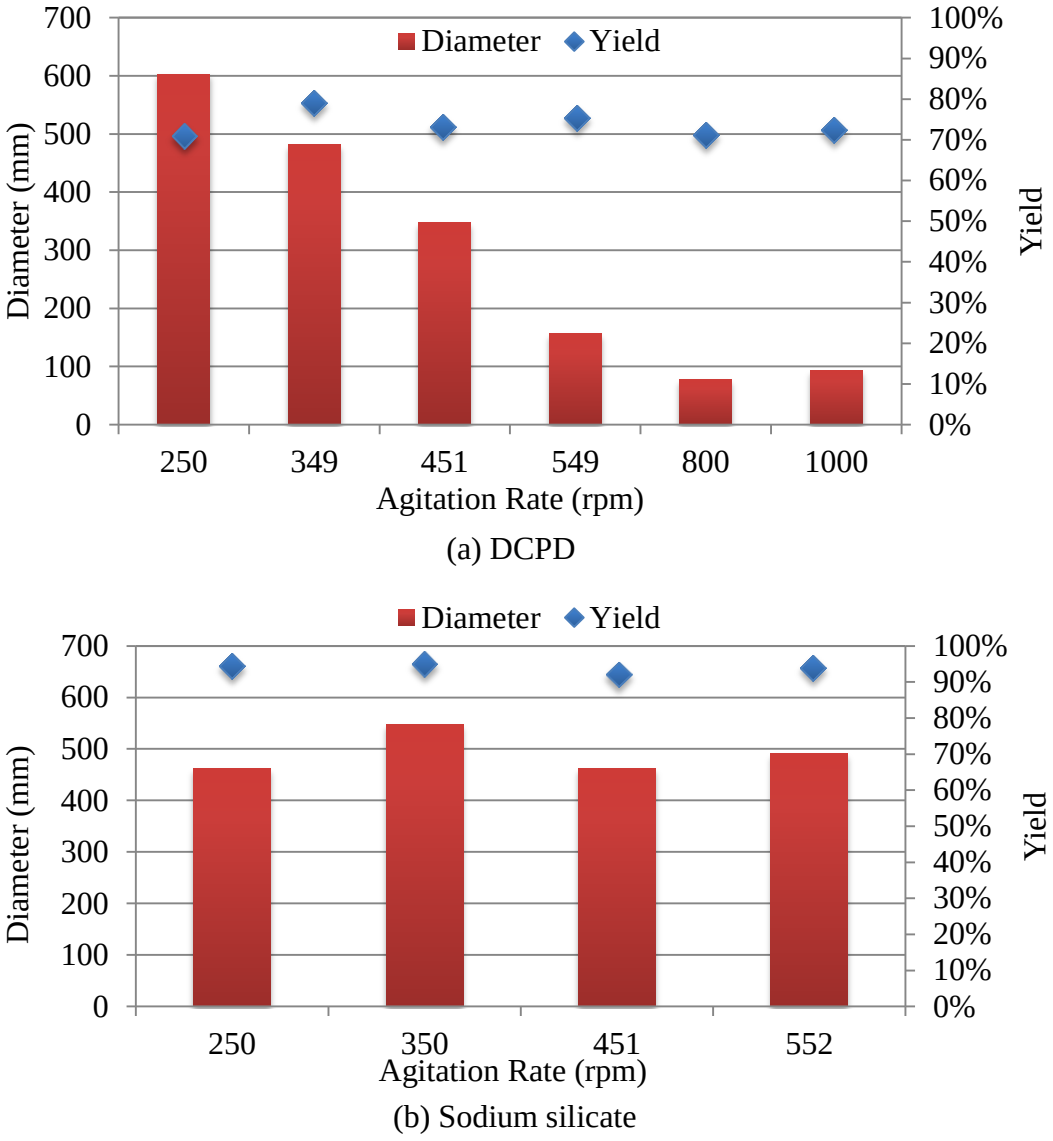
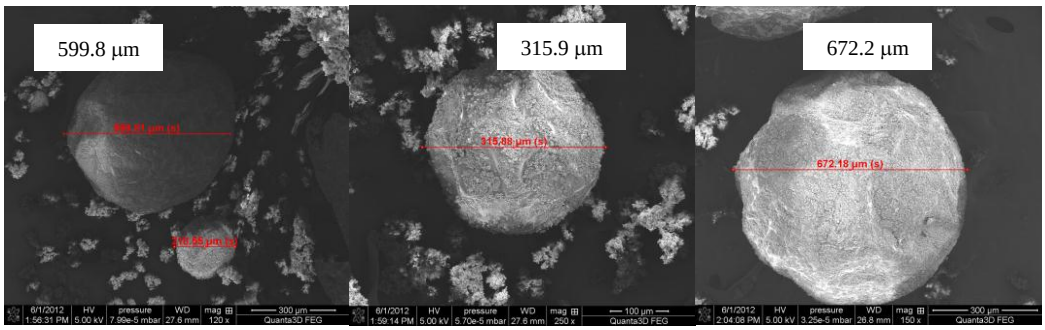
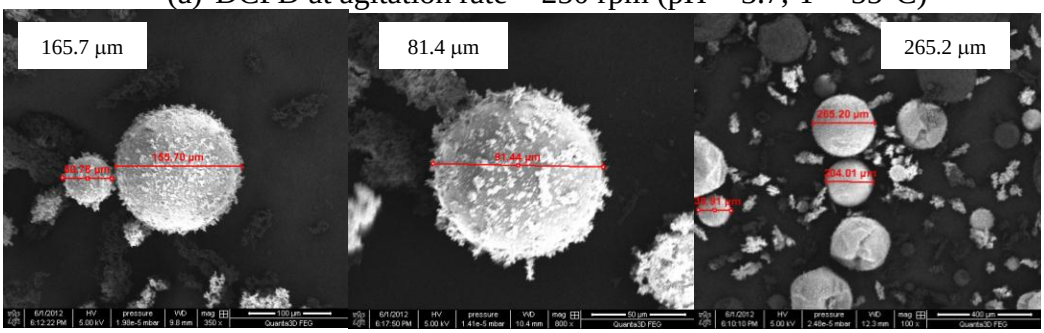


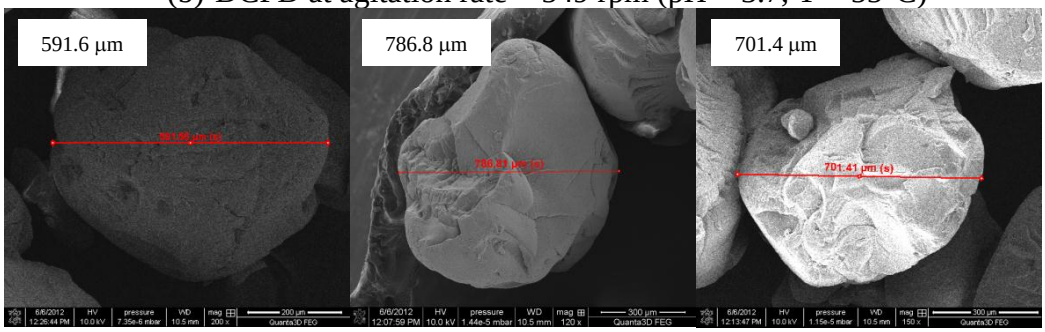
Figure 6: Effect of Agitation Rate on the Diameter for: (a) DCPD Microcapsules, and (b) Sodium Silicate Microcapsules



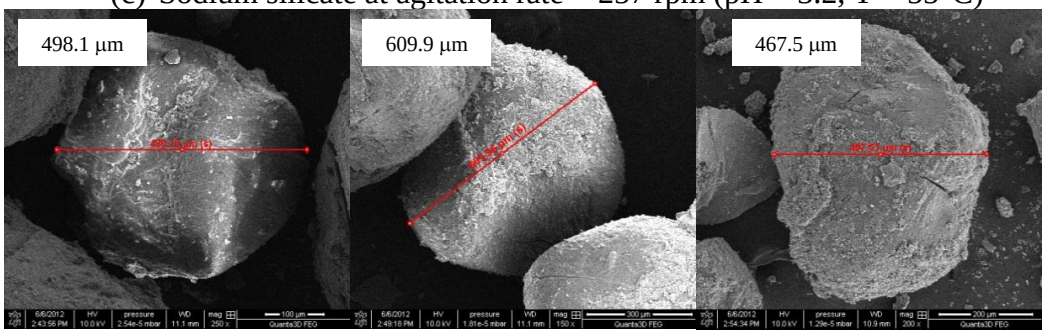
(a) DCPD at agitation rate = 250 rpm (pH = 3.7, T = 55°C)



(b) DCPD at agitation rate = 549 rpm (pH = 3.7, T = 55°C)



(c) Sodium silicate at agitation rate = 257 rpm (pH = 3.2, T = 55°C)



(d) Sodium silicate at agitation rate = 551 rpm (pH = 3.2, T = 55°C)

Figure 7: Effects of Agitation Rate on the Morphology of Microcapsules for: (a) DCPD at 250 rpm, (b) DCPD at 549 rpm, (c) Sodium Silicate at 257 rpm, and (d) Sodium Silicate at 551 rpm

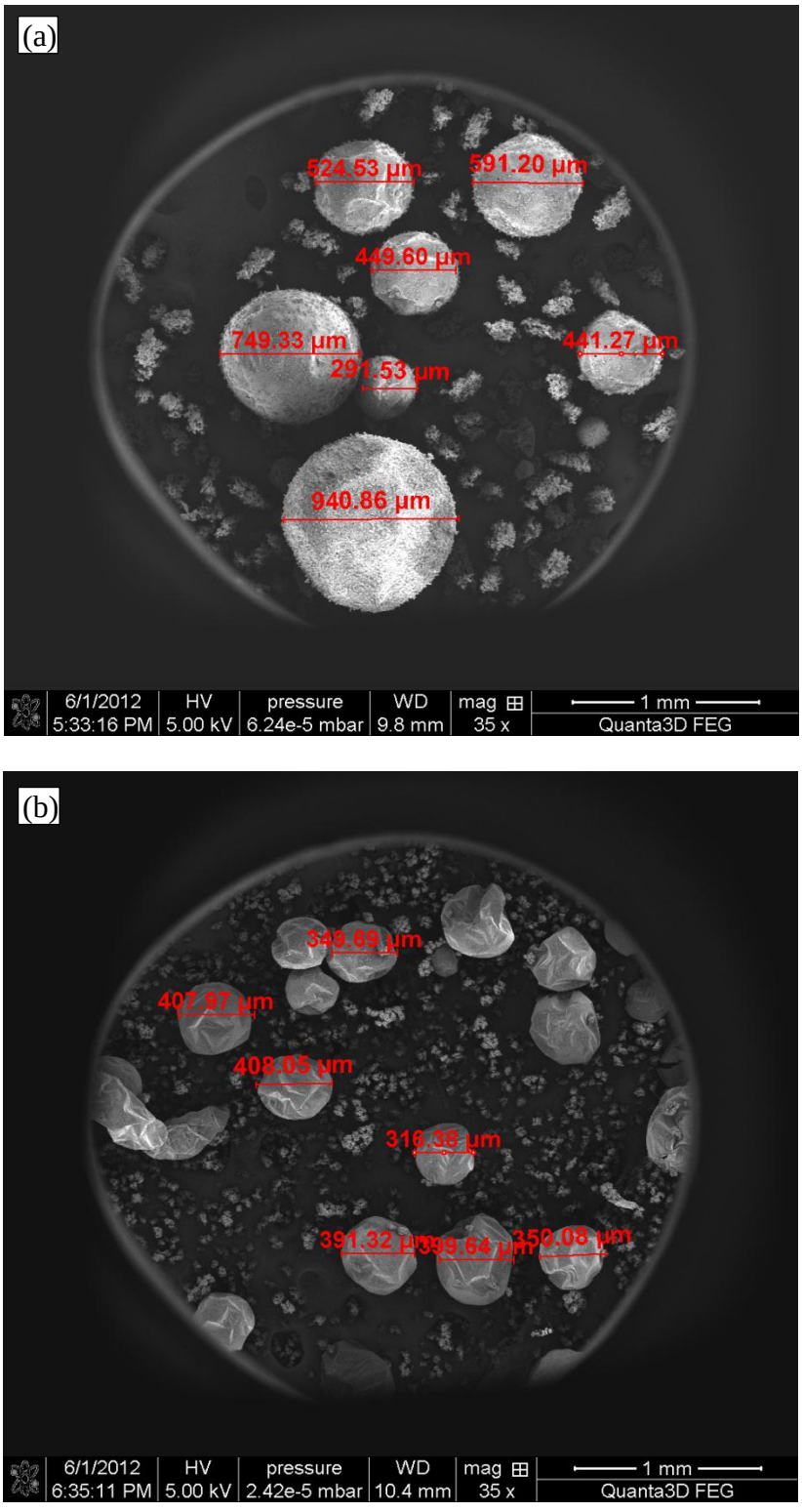


Figure 8: Qualitative Size Distribution for DCPD Microcapsules as a Function of Agitation Rate: (a) 350 rpm, and (b) 450 rpm

4.2 Evaluation of the effects of microcapsules' properties on concrete self-healing mechanism

A set of laboratory tests was performed to measure the modulus of elasticity of plain concrete with and without self-healing microcapsules before and after a 1-week healing period. The objective of this experimental investigation was to obtain preliminary information on the relation between production parameters of the microcapsules of self-healing agents (which affect the morphology and shell thickness of the microcapsules) and the effectiveness of the microcapsules in enhancing the concrete self-healing properties.

Figure 9 presents the effects on the concrete modulus of elasticity before and after healing of DCPD (with a content of 0.25% of the cement weight) and sodium silicate (with a content of 5% of the cement weight) microcapsules prepared at different pH values. Error bars showing the average variability (about ±10%) that was observed in the measurements are also provided.

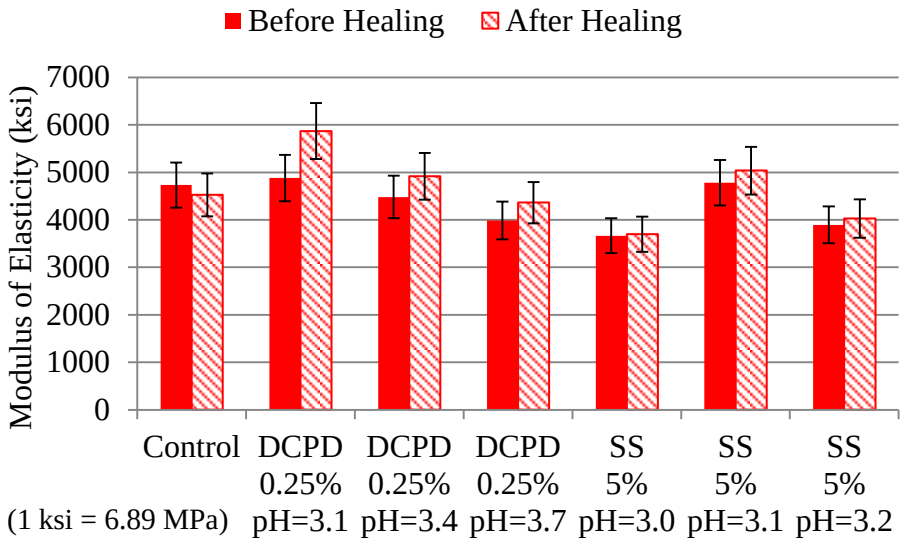


Figure 9: Effect of Preparation pH of Microcapsules on Concrete Modulus of Elasticity before and after Healing

The following observations are made based on the results presented in Figure 9:

1) As expected, no self-healing process was detected for the control specimens (i.e., without self-healing), for which a small decrease of the modulus of elasticity (smaller than the variability of the measurements) was recorded. This result suggests that the control specimens were subjected to a small but not negligible damage, with likely formation of micro-cracks within the specimens.
2) The concrete modulus of elasticity after healing of specimens with DCPD was significantly higher than that before healing. This phenomenon indicates that the self-healing process was activated and that the self-healing material produced a higher stiffness and, as a consequence, a higher strength (which, for concrete, is positively correlated with the stiffness) than those of the original undamaged concrete. This after-healing stiffness increase was more pronounced

for lower values of the pH, which correspond to higher thicknesses of the microcapsules' walls. The best performance of the after-healing concrete was obtained for pH = 3.1.

3) The modulus of elasticity of the concrete with DCPD before healing decreased significantly for increasing pH (i.e., for lower values of the microcapsules' shell thickness). At a pH value of 3.1, the average modulus of elasticity of the specimens with DCPD was almost the same (slightly higher) than that of the specimens of plain concrete, while at a pH value of 3.7 the modulus of elasticity was about 15% lower than that of the plain concrete specimens.

4) Sodium silicate caused a significant decrease in the modulus of elasticity before healing when compared to the control concrete mix for pH values of 3.0 and 3.2, while it did not affect the modulus of elasticity of the specimens for a pH value of 3.1. The data available at this point are insufficient to identify the reason for this trend. The lower stiffness (and strength) of the concrete with sodium silicate before healing should not be a concern as long as the design accounts for the proper values.

5) The modulus of elasticity of the concrete with sodium silicate was higher after healing than before healing for all pH values. The highest increase in the modulus of elasticity was measured for pH = 3.1.

6) The shell thickness of the microcapsules significantly affected both the before and after healing modulus of elasticity of the concrete with sodium silicate self-healing agent. In particular, it appears that too low or too large pH values (i.e., too small or too large shell thicknesses) are detrimental to the performance of both before and after healing concrete. This phenomenon can be explained by noticing that, for too small shell thicknesses, the microcapsules collapsed during mixing of the concrete, while for too large shell thicknesses, the microcapsules were not broken by the concrete micro-cracks and, thus, the self-healing agent was not activated. Among the pH values considered in this study, pH = 3.1 provides the best performance for the concrete with sodium silicate.

Figure 10 shows the effects on the concrete modulus of elasticity before and after healing of DCPD (with a content of 0.25% of the cement weight) and different contents of sodium silicate (i.e., 0.5%, 1%, 2.5%, and 5% of the cement weight) microcapsules. Error bars showing the average variability (about ±10%) that was observed in the measurements are also provided. It was observed that the concrete modulus of elasticity after healing increased for all specimens with self-healing agents, with the exception of specimens with sodium silicate content equal to 0.5%. This result suggests that such low content of sodium silicate was insufficient to provide adequate healing that can enhance the capacity of the prepared concrete. The DCPD self-healing action was very effective even at the very low content considered in this research, i.e., 0.25%. In addition, DCPD did not affect negatively the modulus of elasticity of the concrete before healing. The presence of sodium silicate microcapsules reduced the modulus of elasticity of the concrete before healing, with the exception of the specimens with sodium silicate content equal to 5%, for which the modulus of elasticity was practically the same as for the plain concrete. From the results presented in Figure 9 and Figure 10, for sodium silicate microcapsules, the best performance of the concrete before and after healing was found for a pH of 3.1 and a content of 5%.

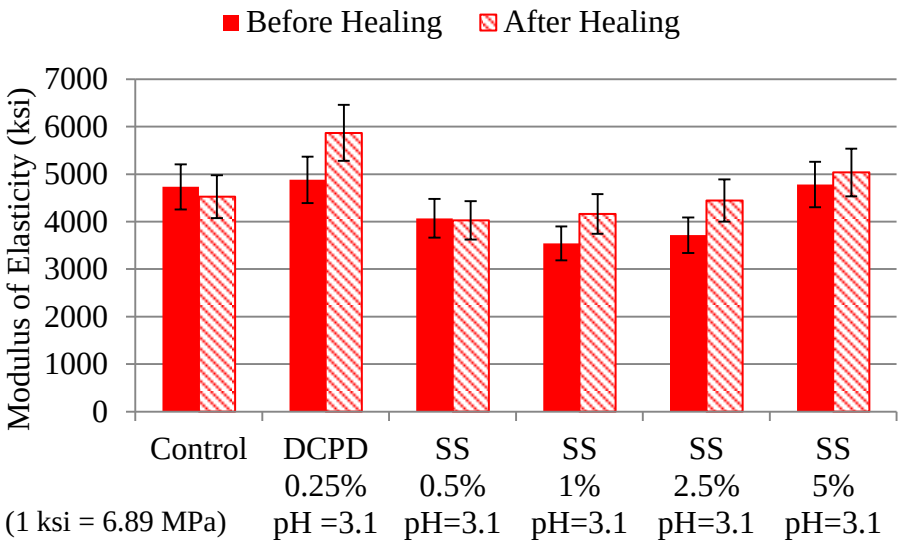
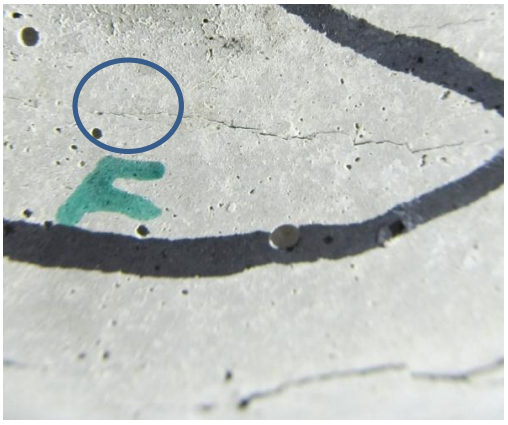
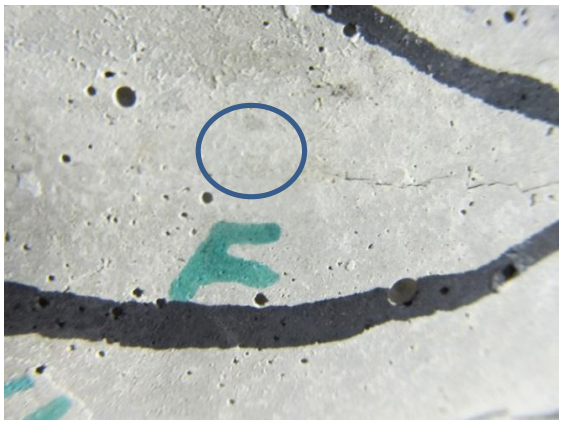


Figure 10: Effect of Amount of Microcapsules (% of Cement Weight) on Concrete Modulus of Elasticity before and after Healing

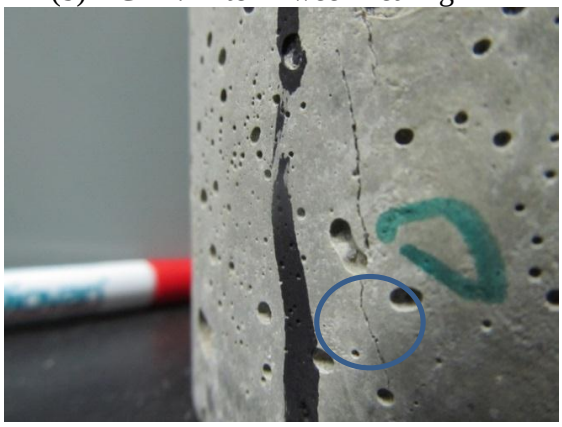


(a) DCPD: Before healing



(b) DCPD: After 1-week healing

(c) Sodium silicate: Before healing



(d) Sodium silicate: After 1-week healing

Figure 11: Crack Healing after 1-Week Recovery: (a) DCPD before Healing, (b) DCPD after 1-Week Healing, (c) Sodium Silicate (1%) before Healing, and (d) Sodium Silicate (1%) after 1-Week Healing

Specimens that cracked during testing were used to visually observe crack healing. Figure 11 presents a visual inspection of a cracked specimen before and after 1-week healing of the concrete prepared with 0.25% DCPD (pH = 3.4) and 5.0% sodium silicate (pH = 3.1). These pictures were taken under the same environmental conditions. This figure shows that a portion of the surface crack healed due to the presence of the self-healing agent, which was released into the crack after the microcapsules were broken due to the stresses produced by the concrete cracks. From these results, it appears that DCPD-based microcapsules were effective in healing the cracks in the concrete specimens. It is noted that microcapsules are designed to heal small cracks (micro-cracks) and this approach does not appear to be effective in healing of large cracks.

4.3 Evaluation of FRP-confinement effects on self-healing concrete

A set of laboratory tests was performed to measure the stress-strain behavior of self-healing concrete subject to quasi-static cyclic loading. The self-healing agent considered in this research task was sodium silicate, which was added to the concrete mix as 1%, 2.5%, and 5% of cement weight. Both plain (unconfined) and FRP-confined concrete specimens were considered. Using the experimental stress-strain curves, the residual and maximum strains at each load cycle, as well as the stiffness modulus, were computed to examine and compare the effects of self-healing.

Table 5 provides the residual ("Resid.") and maximum ("Max.") strains for all load cycles of every concrete specimen tested in Task 3 of this research project. Two of the specimens (i.e., SH00PL #3 and SH01PL #3) were damaged and were not tested under cyclic loading. The residual and maximum strains are indirect indications of the damage level of the concrete specimen. The results present a significant scatter. It is observed that the maximum strains before and after healing tend to be very similar. The maximum strains after healing are usually slightly smaller than the corresponding strains before healing, with the exception of the specimens with 2.5% sodium silicate, for which the opposite is true. The strains corresponding to specimens with 1% sodium silicate are usually larger than the corresponding strains of specimens with other sodium silicate content. The combination of FRP-confinement and 5% sodium silicate seems to be particularly efficient in reducing both the residual and the maximum strains.

Figures 12 through 15 compare the stress-strain response before and after healing of one unconfined and FRP-confined specimen for each sodium silicate content considered in this study. It is observed that, in general, the stress-strain curves after healing and before healing are closer when FRP-confinement is employed rather than when the concrete is unconfined. In addition, the specimens with 1% sodium silicate reach a higher level of damage when compared to specimens with other sodium silicate content. In contrast, the specimens with 5% sodium silicate are the least damaged among all the specimens. In addition, the stress-strain curves before and after healing are most similar for the specimens with 5% sodium silicate. These observations are consistent with the results obtained in Task 2 of this research and seem to suggest that the addition of 1% sodium silicate decreases the strength and stiffness of the concrete, whereas the addition of 5% sodium silicate decreases the strength and stiffness of the concrete.

Load cycle			#1 (20%)		#2 (40%)		#3 (75%)		#4 (75%)		#5 (75%)	
ID	#	Healing	Resid. (10^{-3} in/in)	Max. (10^{-3} in/in)	Resid. (10^{-3} in/in)	Max. (10^{-3} in/in)	Resid. (10^{-3} in/in)	Max. (10^{-3} in/in)	Resid. (10^{-3} in/in)	Max. (10^{-3} in/in)	Resid. (10^{-3} in/in)	Max. (10^{-3} in/in)
SH00PL	1	Before	0.031	0.260	0.029	0.524	0.084	1.076	0.061	1.088	0.077	1.078
		After	0.071	0.290	0.070	0.571	0.083	1.081	0.091	1.090	0.105	1.090
	2	Before	0.038	0.260	0.052	0.548	0.117	1.108	0.133	1.156	0.145	1.160
		After	0.031	0.286	0.038	0.577	0.064	1.108	0.074	1.125	0.079	1.135
SH00FRP	1	Before	0.039	0.319	0.066	0.696	0.042	1.347	0.265	1.401	0.299	1.467
		After	0.044	0.354	0.059	0.718	0.107	1.251	0.129	1.280	0.150	1.322
	2	Before	0.032	0.299	0.044	0.640	0.112	1.196	0.133	1.237	0.154	1.267
		After	0.035	0.327	0.041	0.684	0.094	1.229	0.110	1.255	0.116	1.277
	3	Before	0.042	0.313	0.059	0.654	0.122	0.991	0.105	1.218	0.128	1.254
		After	0.030	0.315	0.031	0.658	0.070	1.159	0.081	1.190	0.092	1.220
SH01PL	1	Before	0.033	0.287	0.047	0.601	0.128	1.266	0.148	1.295	0.147	1.311
		After	0.035	0.320	0.048	0.652	0.098	1.248	0.117	1.279	0.131	1.299
	2	Before	0.037	0.294	0.060	0.630	0.196	1.409	0.097	1.336	0.123	1.372
		After	0.033	0.316	0.037	0.634	0.077	1.209	0.076	1.230	0.076	1.240
SH01FRP	1	Before	0.063	0.341	0.095	0.729	0.349	1.599	0.468	1.796	0.570	1.963
		After	0.065	0.448	0.105	0.937	0.275	1.735	0.357	1.869	0.351	1.958
	2	Before	0.043	0.337	0.079	0.718	0.052	1.511	0.345	1.628	0.280	1.728
		After	0.060	0.404	0.102	0.857	0.186	1.503	0.215	1.607	0.260	1.681
	3	Before	0.057	0.346	0.089	0.739	0.243	1.464	0.304	1.572	0.351	1.650
		After	0.057	0.365	0.084	0.777	0.191	1.424	0.228	1.487	0.261	1.540
SH25PL	1	Before	0.036	0.227	0.047	0.472	0.100	0.951	0.113	0.968	0.129	0.988
		After	0.030	0.286	0.039	0.592	0.087	1.235	0.091	1.244	0.104	1.286
	2	Before	0.032	0.240	0.047	0.507	0.112	1.032	0.129	1.053	0.137	1.059
		After	0.034	0.292	0.044	0.598	0.105	1.266	0.123	1.299	0.118	1.342
	3	Before	0.027	0.277	0.035	0.575	0.102	1.176	0.113	1.201	0.115	1.208
		After	0.038	0.295	0.056	0.643	0.109	1.243	0.137	1.300	0.153	1.334
SH25FRP	1	Before	0.041	0.327	0.062	0.680	0.135	1.219	0.158	1.281	0.166	1.299
		After	0.046	0.350	0.062	0.710	0.098	1.252	0.113	1.284	0.118	1.295
	2	Before	0.046	0.334	0.066	0.692	0.127	1.258	0.144	1.297	0.171	1.334
		After	0.048	0.371	0.064	0.749	0.109	1.317	0.122	1.345	0.132	1.370
	3	Before	0.026	0.306	0.027	0.639	0.085	1.186	0.100	1.205	0.102	1.221
		After	0.050	0.353	0.065	0.722	0.097	1.246	0.105	1.276	0.118	1.298
SH50PL	1	Before	0.049	0.267	0.063	0.552	0.121	1.076	0.134	1.090	0.139	1.096
		After	0.042	0.285	0.038	0.568	0.050	1.068	0.052	1.073	0.058	1.076
	2	Before	0.027	0.253	0.027	0.518	0.059	1.030	0.065	1.038	0.048	1.071
		After	0.032	0.267	0.035	0.541	0.053	1.012	0.052	1.013	0.052	1.012
	3	Before	0.042	0.256	0.049	0.534	0.082	1.053	0.087	1.058	0.093	1.069
		After	0.033	0.286	0.035	0.557	0.057	1.046	0.069	1.061	0.073	1.062
SH50FRP	1	Before	0.055	0.297	0.067	0.628	0.086	1.129	0.098	1.148	0.106	1.164
		After	0.047	0.336	0.043	0.665	0.069	1.132	0.075	1.135	0.084	1.149
	2	Before	0.076	0.310	0.095	0.676	0.119	1.160	0.088	1.142	0.097	1.153
		After	0.046	0.339	0.053	0.682	0.075	1.167	0.086	1.183	0.105	1.206
	3	Before	0.062	0.272	0.117	0.590	0.225	1.078	0.287	1.138	0.316	1.157
		After	0.043	0.329	0.041	0.649	0.058	1.109	0.067	1.122	0.079	1.140

Table 5: Residual and maximum strains at each load cycle of tested concrete specimens

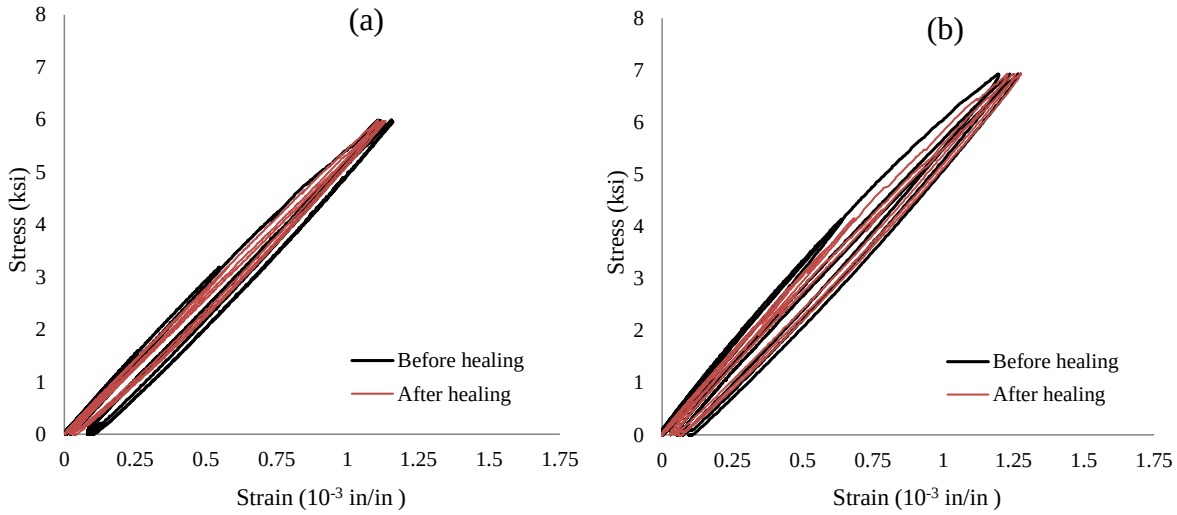


Figure 12: Stress-Strain Response for Plain Concrete Specimens: (a) Unconfined, and (b) FRP-Confined

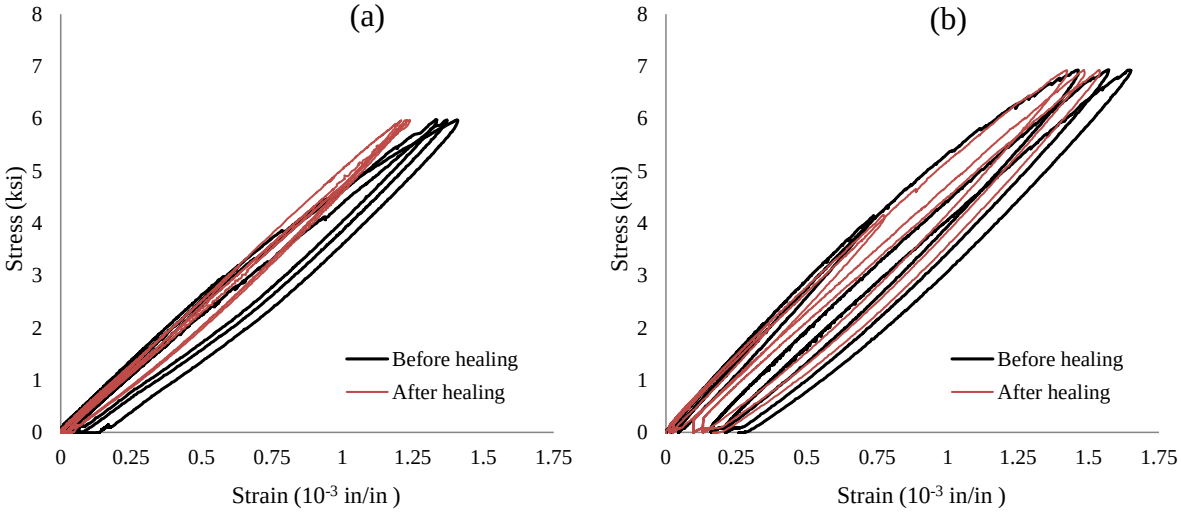


Figure 13: Stress-Strain Response for Concrete Specimens with 1.0% Sodium Silicate: (a) Unconfined, and (b) FRP-Confined

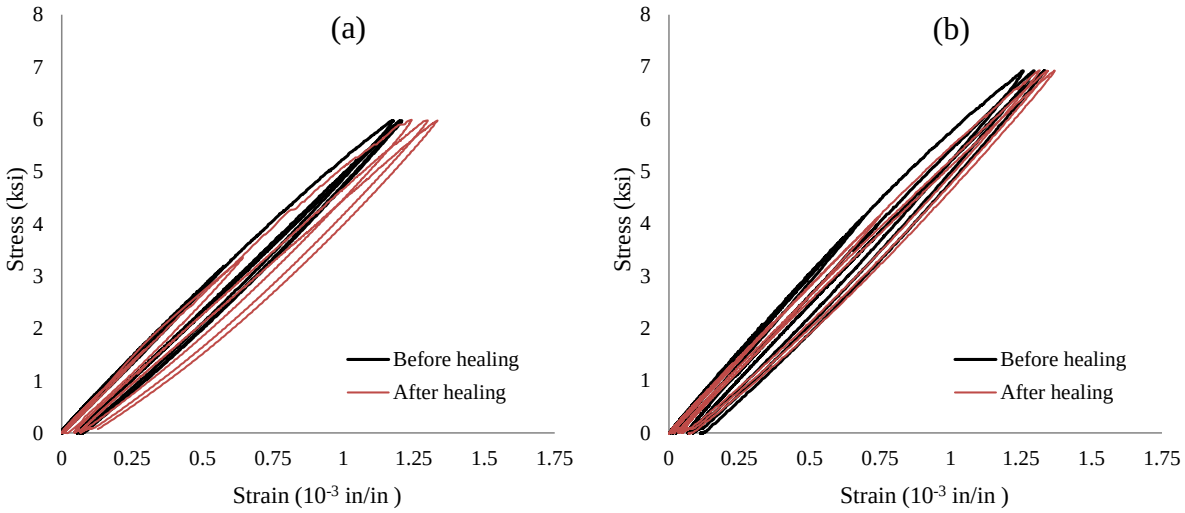


Figure 14: Stress-Strain Response for Concrete Specimens with 2.5% Sodium Silicate: (a) Unconfined, and (b) FRP-Confined

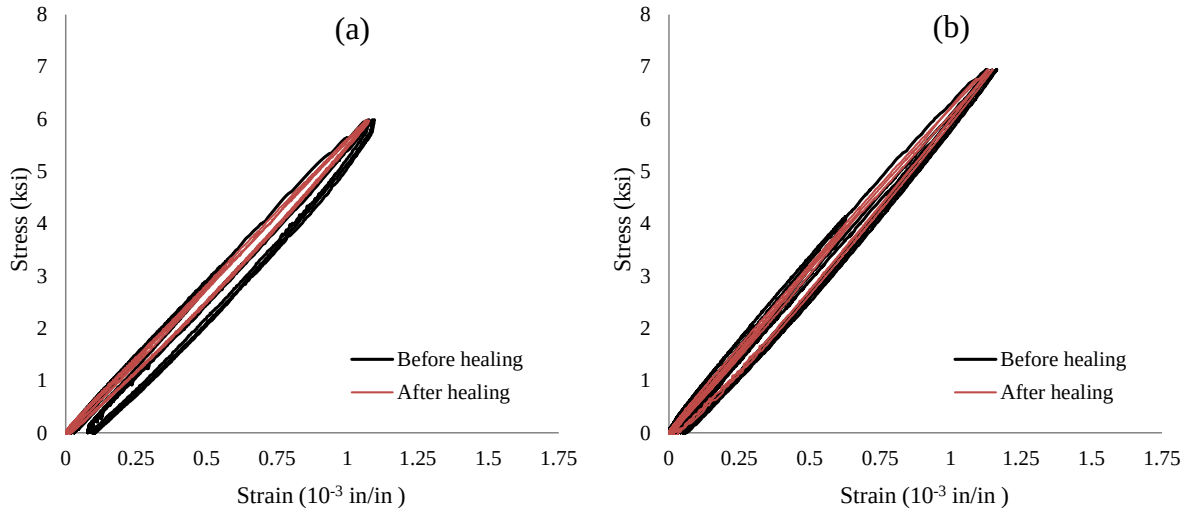


Figure 15: Stress-Strain Response for Concrete Specimens with 5.0% Sodium Silicate: (a) Unconfined, and (b) FRP-Confined

Figure 16 shows the values of the stiffness at low levels of stress for the tested concrete specimens. This stiffness is obtained as the average of the secant stiffnesses computed between 2% and 10% of the estimated peak strength (1) in the first two loading cycles of the loading procedure before healing (undamaged material), (2) in the last two cycles of the loading procedure before healing (damaged material), and (3) in the first two cycles of the loading procedure after healing (material after healing). Also in this case, a non-negligible variability of the results was observed. In general, the specimens with FRP-confinement were stiffer than the corresponding unconfined specimens, with the exception of the specimens with 2.5% sodium silicate. In terms of stiffness recovery, a similar behavior was observed for both unconfined and

FRP-confined specimens. In addition, only a null or minimal stiffness recovery was found after a one-week healing period for the specimens. This observation indicates that other unaccounted for variables determined the stiffness recovery behavior rather than the presence of FRP-confinement. Possible explanations for the non-activation of the self-healing mechanisms may be: chemical degradation of the microcapsules due to the basic environment inside the concrete, insufficient humidity to allow for sodium silicate reaction within the concrete, and/or excessive size of micro-cracking (due to the fact that higher stress levels were reached in Task 3 of this research).

The results obtained in Task 3 of this research project regarding stiffness recovery alone are insufficient to prove or disprove the hypothesis that composite action can increase the efficiency of self-healing mechanisms in the concrete. Additional analysis of the collected data is ongoing to gain additional insight into the problem at hand and to develop a research plan that will be able to reliably test the hypothesis that composite action can improve the self-healing properties of self-healing concrete.

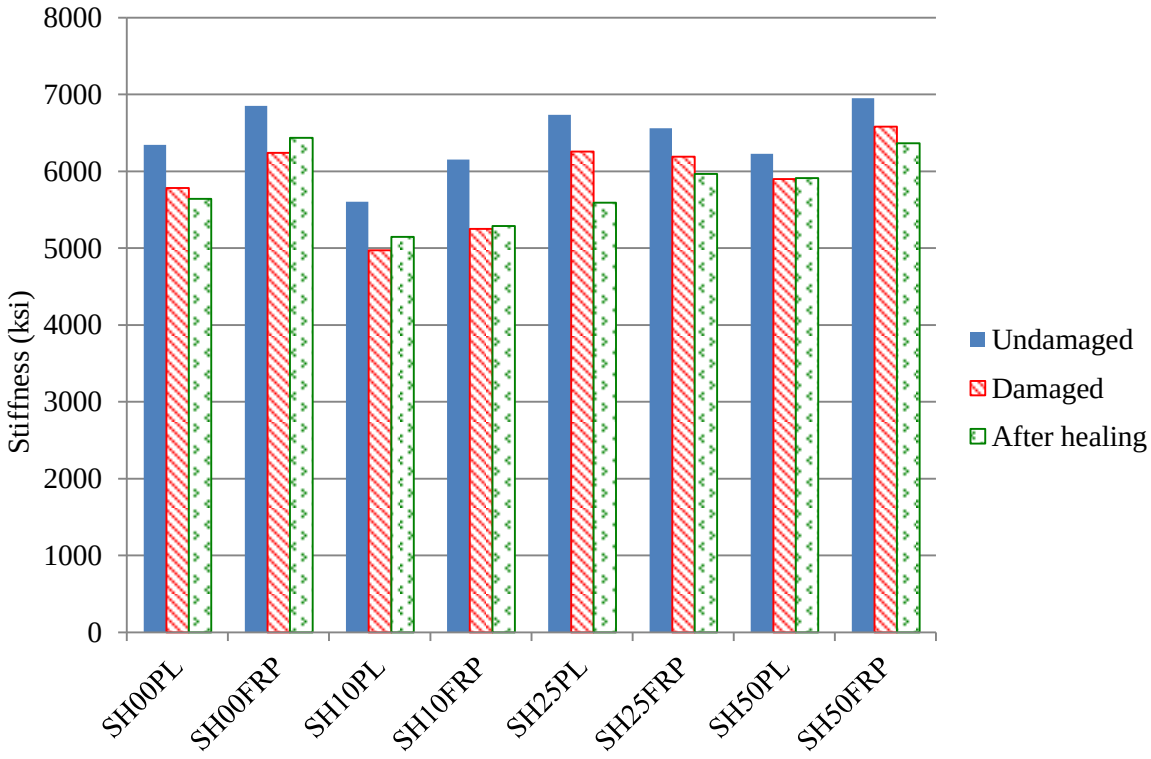


Figure 16: Concrete Stiffness Before and After Healing

5 Conclusions

The objectives of this study were: (1) to evaluate the effects of preparation parameters (namely, temperature, agitation rate, and pH) on the shell thickness and size (diameter) of healing agent

microcapsules for use in self-healing concrete; (2) to evaluate the effects of microcapsules' shell thicknesses and size diameters on the concrete self-healing mechanism; and (3) to test the hypothesis that composite action due to FRP confinement of cylindrical concrete specimens can improve the self-repairing properties of self-healing concrete materials. Two healing agents were evaluated for the first two objectives of this study, i.e., DCPD and sodium silicate. The use of sodium silicate was considered for the third objective of this study. Based on the results of the experimental program, the following conclusions were made:

1) As the pH was reduced, the shell thickness of the DCPD microcapsules increased. Unlike DCPD, the shell thickness of sodium silicate microcapsules increased for increasing pH. The shell thickness of sodium silicate microcapsules was almost twice the shell thickness of DCPD microcapsules.
2) The more uniform and coherent microcapsules were produced at a temperature of 55°C for both DCPD and sodium silicate healing agents. For the DCPD microcapsules, the solution remained an emulsion and no encapsulation took place at 49°C. For sodium silicate, no microcapsules were formed at 53°C.
3) The increase in agitation rate resulted in a decrease in the average diameter of the microcapsules for DCPD. By contrast, the diameter of the microcapsules remained almost constant for sodium silicate microencapsulation as the agitation rate increased.
4) DCPD-based microcapsules were effective in increasing the concrete modulus of elasticity after healing, even at content as low as 0.25% of cement weight. For sodium silicate, an optimum pH value and content needs to be identified in order to produce microcapsules that enhance the concrete modulus of elasticity before and after healing. From the results presented in this study, a pH value of 3.1 at a sodium silicate content of 5.0% was found to provide the best performance.
5) The use of FRP confinement generally improved the performance of the concrete. However, the self-healing effects in terms of stiffness recovery observed in Task 3 of this project were null or very small for both unconfined and FRP-confined specimens. Thus, the data collected in this research in terms of stiffness recovery alone are insufficient to prove or disprove the hypothesis that composite action can increase the efficiency of self-healing mechanisms in the concrete.

Appendix A: DCPD Microencapsulation Procedure

The adopted procedure was performed by using in-situ polymerization, in an oil-in-water emulsion. The main steps of this procedure can be summarized as follows:

1) Place 200 ml of Deionized (DI) water in a 1000 ml beaker;
2) Dissolve 50 ml of 2.5 wt.% EMA copolymer using a magnetic stirrer and ultra sound water bath to develop an aqueous solution;

3) Agitate using a IKA RW 20 digital mixer, with a driving 55 mm low shear three-bladed mixing propeller placed just above the bottom of the beaker;
4) Under agitation, add 5.00 g urea, 0.50 g resorcinol and 0.50 g ammonium chloride in the solution;
5) Set the pH by using sodium hydroxide (NaOH) and hydrochloric acid (HCl) drop-wise with a disposable pipet;
6) Add two to three drops of 1-octanol to reduce surface bubbles;
7) Allow the solution to stabilize for approximately 6 – 8 minutes at the appropriate pH and rpm agitation rate, before 100 ml of DCPD is added at a slow stream rate;
8) Allow the solution to stabilize for 13 – 15 minutes before 12.7 g of 37 wt% aqueous solution of formaldehyde was added to the emulsion;
9) Wrap and cover the solution with aluminum foil, and slowly heat to the set temperature;
10) Turn off the hot plate after 4 hours of continuous agitation;
11) Once cooled to ambient temperature, the suspension of microcapsules was separated under vacuum filtration;
12) Rinse microcapsules with DI water three times with 500 ml of DI water, and then allow to air dry for 48 - 72 h.

Appendix B: Sodium Silicate Microencapsulation Procedure

This procedure was accomplished by using in-situ polymerization, in an oil-in-water emulsion. The main steps of this procedure can be summarized as follows:

1) Place 200 ml of DI water in a 1000 ml beaker;
2) Dissolve 50 ml of 2.5 wt.% EMA copolymer using a magnetic stirrer and ultra sound water bath to develop an aqueous solution;
3) Agitate using a IKA RW 20 digital mixer, with a driving 55 mm low shear three-bladed mixing propeller placed just above the bottom of the beaker;
4) Under agitation, add 5.00 g urea, 0.50 g resorcinol and 0.50 g ammonium chloride;
5) Set the pH by using sodium hydroxide (NaOH) and hydrochloric acid (HCl) drop-wise with a disposable pipet;
6) Add two to three drops of 1-octanol to reduce surface bubbles;
7) Allow the solution to stabilize for approximately 6 – 8 minutes at the appropriate pH and rpm agitation rate;
8) Mix 170 ml of DI water with 60 ml of an aqueous sodium silicate and add to the solution;

9) Agitate the solution for approximately 5 min. While under agitation, HCL was slowly added to the solution to form a gel/aqueous solution;

10) Add 100 ml of the gel/aqueous solution to the emulsion while maintaining a pH of 3.0 – 3.5;

11) Allow the solution to stabilize for 13 – 15 minutes before 12.7 g of 37 wt% aqueous solution of formaldehyde was added to the emulsion;

12) Wrap and cover the solution with aluminum foil, and slowly heat to the set temperature;

13) Turn off the hot plate after 4 hours of continuous agitation;

14) Once cooled to ambient temperature, the suspension of microcapsules was separated under vacuum filtration;

15) Rinse microcapsules with DI water three times with 500 ml of DI water, and then allow to air dry for 48 - 72 h.

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